Indian J. Phys. **76A** (6), 573-576 (2002)

IJP A
an international journal

Statistics of closed multi-component system : Entropy, fluctuation and stability

C G Chakrabarti* and Milan Kumar De

Department of Applied Mathematics, University of Calcutta, Kolkata – 700 009, India

E mail : cgc-math@rediffmail.com

Received 10 June 2002, accepted 9 August 2002

Abstract : The paper deals with the derivation of the probability distribution of a closed multi-component system, the expression of entropy-production for chemical reaction, the criterion of chemical stability and the generalized Le-Chatelier-Braun principle of chemical equilibrium on the basis of a probabilistic model of the closed multi-component system

Keywords : Closed multi-component systems, maximum-entropy principle, probability distribution, entropy-production, chemical stability

PACS Nos. : 05.70.Ln, 05.20.-y

1. Introduction

A multi-component system is composed of a multiple of components, for example a system of chemically reacting substances, or a biological community consisting of a number of interacting ecological species. A multi-component system may be closed, the total number of molecules (or moles) being fixed. It may be open, and the total number of molecules (or moles) not being fixed, the system can exchange not only energy but also matter (molecules) with the environment. A multi-component system undergoes changes due to the changes in the molecular numbers brought about by chemical reactions. Thermodynamics of multi-component system is well-developed and plays a significant role in the theoretical foundation of chemistry [1].

In the present paper, we shall develop a statistical theory of a closed multi-component system. This includes the derivation of the probability distribution of the molecular numbers, the expression of entropy-production (or entropy-change), the probability of fluctuation near stationary equilibrium state and finally the criterion of chemical stability and the Le-Chatelier-Braun principle of stability of chemical equilibrium from the consideration of the probability of fluctuation.

*Corresponding Author

2. Closed multi-component system : probability distribution

Let us first consider a closed multi-component system consisting of n chemically reacting substances or species. Let N_i (i = 1,2,3 .....n) be the number of molecules of the ith substances or species maintained at uniform temperature T. It is assumed that the reactions proceed sufficiently slowly so as not to disturb seriously the equilibrium energy distribution of each component to any appreciable extent [2]. The total number of molecules constituting the system $\sum_{i=1}^{n} N_i = N$ is fixed :

The macroscopic state of the system is given by the set of molecular numbers $A_n = \{N_1, N_2, \ldots N_n\}$. We assume that the system obeys classical statistics. The statistical weight or thermodynamic probability of the macroscopic state A_n is given by

$$W(A_n) = W(N_1, N_2, \ldots, N_n) = \frac{N!}{\prod_{i=1}^{n} N_i} \tag{2.1}$$

which is the total number of microscopic states or complexions compatible with the macroscopic state of the system. The thermodynamic probability is not a probability at all. It is an

integer [3]. We are, however interested in the determination of the probability distribution $P(A_n) = P(N_1, N_2, ..., N_n)$ of the macroscopic state $A_n = \{N_1, N_2, ..., N_n\}$ on the basis of prior information or data The molecular numbers $\{N_1, N_2, ..., N_n\}$ are assumed to the random variables and this is due to the manifestation of many body aspect of the system under consideration.

Let the information available about the system be the average molecular numbers.

$$\sum N_i P(N_1, N_2, \ldots, N_n) = \bar{N}_i, (i = 1,2,\ldots,n), \quad (2.2)$$

where $R_{N,n}$ is the set of non-negative integral solution of the equation

$$N_1 + N_2 + \ldots + N_n = N, \quad (N_i \geq 0). \quad (2.3)$$

The averages $\bar{N}_i$ given by (2.2) constitute the prior information about the system. We have to estimate the probability $P(N_1, N_2, \ldots, N_n)$ on the basis of these information. For this we shall make use of the principle of maximum entropy estimation [4] which consists of the maximization of Bayesian entropy [5].

$$S_B = -\sum_{R_{N,n}} P(N_1, N_2, \ldots, N_n) \ln \frac{P(N_1, N_2, \ldots, N_n)}{W(N_1, N_2, \ldots, N_n)} \quad (2.4)$$

subject to the constraints (2.2) and the normalization condition

$$\sum_{R_{N,n}} P(N_1, N_2, \ldots, N_n) = 1. \quad (2.5)$$

It may be noted that the measure $W(N_1, N_2, \ldots, N_n)$ is the prior information about the macrostate $A_n = \{N_1, N_2, \ldots, N_n\}$ of the system and for the system under consideration it is given by (2.1). The maximization of (2.4) subject to the constraints (2.2) and (2.5) leads to the multinomial distribution

$$P(A_n) = P(N_1, N_2, \ldots, N_n) = \frac{N!}{\prod_{i=1}^{n} N_i} \prod_{i=1}^{n} (p_i^0)^{N_i}, \quad (2.6)$$

where p_i^0's are the prior probability that a molecule belongs to the ith subsystem or species and they are to be determined from the prior information or constraints (2.2). Assuming N_i (i = 1, 2, ..n) to be very large, we can reduce ; using Stirling's approximation, the logarithm of the probality $P(N_1, N_2, \ldots, N_n)$ to the form

$$\ln P(N_1, N_2, \ldots, N_n) = -N \sum_{i=1} p_i \ln \frac{p_i}{p_i^0}, \quad (2.7)$$

where $p_i = \frac{N_i}{N}$ is the relative frequency of the i-th substance or species and for large N, p_i is the probability that a molecule selected at random falls in the i-th species. Except for the multiplicative constant ($-N$), the right hand side of (2.7) is known as Kullback [6] measure of discrimination information or cross-entropy between the probability distribution $\{p_1, p_2, \ldots, p_n\}$ and $\{p_1^0, p_2^0, \ldots, p_n^0\}$. For multinomial distribution (2.6) the average $\bar{N}_i$ are given by $\bar{N}_i = Np_i^0$ ($i = 1, 2, \ldots, n$) so that the "a priori" probabilities p_i^0 can be estimated by $p_i^0 = \frac{\bar{N}_i}{N}$. Replacing p_i and p_i^0 by $\frac{N_i}{N}$ and $\frac{\bar{N}_i}{N}$ respectively, we have

$$\ln P(A_n) = \ln P(A_1, A_2, \ldots, A_n) = -\sum_{i=1}^{n} N_i \ln \frac{N_i}{N} \quad (2.8)$$

which is a measure of relative entropy defined over the set of non-negative integers $R_{N,n}$. The averages $\bar{N}_i$ are the stationary equilibrium values of N_i ($i = 1,2,\ldots,n$) [7]. The right-hand side of (2.8) except for a multiplicative constant is, (as we shall show in the next section),the entropy produced within the closed system during transition from the stationary equilibrium state $\{\bar{N}_1, \bar{N}_2, \ldots, \bar{N}_n\}$ to the non-stationary state $\{N_1, N_2, \ldots, N_n\}$

3. Chemical reaction : entropy-production

Let us now study the thermodynamic significance of the right hand side of (2.8) We assume that the system under consideration is an ideal gas mixture [8] and consider a transition of the system from the stationary equilibrium state to the neighbouring non-equilibrium state. Then from Gibbs relation, the change in entropy ds is given by [9],

$$dS = \frac{1}{T} dU + \frac{pdV}{T} - \sum_{i=1}^{n} \frac{\mu_i}{T} dN_i = \frac{dQ}{T} - \sum_{i=1}^{n} \frac{\mu_i}{T} dN_i \quad (3.1)$$

The system being assumed to be enclosed in a fixed volume V, we have $dQ = 0$ so that the change in entropy is given by

$$dS = -\sum_{i=1} \frac{\mu_i}{T} dN_i, \quad (3.2)$$

while the system being assumed to be an ideal gas mixture, the chemical potential μ_i of the i-th species or component is given by [8].

$$\mu_i = \mu_{i0} + KT \ln \frac{N_i}{\bar{N}_i} \quad (3.3)$$

where μ_{i0} is the thermodynamic equilibrium value of μ_i. Assuming (3.2) and (3.3), the rate of entropy production is given

$$\frac{d_i S}{dt} = -K\sum_{i=0}^{n}\left(\ln\frac{N_i}{\bar{N}_i}\right)\frac{dN_i}{dt}$$

$$= -K\sum_{i=1}^{n}\mu_i\frac{dN_i}{dt}$$

$$= -K\sum_{i=1}^{n}\left[\mu_{i0} + KT\ln\frac{N_i}{\bar{N}_i}\right]\frac{dN_i}{dt} \tag{3.4}$$

Integrating (3.4) from the stationary equilibrium state $\{\bar{N}_1, \bar{N}_2, \ldots, \bar{N}_n\}$ to the non-stationary state $\{N_1, N_2, \ldots, N_n\}$ and remembering that $\sum N_i = \sum \bar{N}_i$ we have,

$$S - S_{eq} = \Delta S = -K\sum_{i=1} N_i \ln\frac{N_i}{\bar{N}_i} \tag{3.5}$$

which is the expression of entropy-produced or entropy change [10] Thus the r.h.s. of (2.8) is nothing but the expression of entropy-production (except a multiplicative constant) for a closed multi-component system. As an illustrative example, let us consider a simple chemical reaction model.

We consider an ideal gas reaction in a closed system at uniform temperature T and volume V and let the reaction be the first-order represented by

$$X \leftrightarrow Y. \tag{3.6}$$

The differential of the entropy-change or entropy-production according to (3.5) is given by

$$dS = -K\sum_{i=1}^{n} dN_i \ln\frac{N_i}{\bar{N}_i} \tag{3.7}$$

On the other hand, the degree of advancement ξ is defined by the relation [8].

$$dN_i = \nu_i\, d\xi, \tag{3.8}$$

where ν_i are the stoichiometric coefficients appearing in a chemical equation. For the reaction under consideration :

$$\nu_X = 1, \nu_Y = -1.$$

Then we can write (3.7) in the form

$$dS = -\frac{1}{T}\left\{KT\ln\frac{N_X}{\bar{N}_I} - K\ln\frac{N_Y}{\bar{N}_Y}\right\}d\xi. \tag{3.9}$$

For the ideal gas mixture using the relation (3.3), we have

$$dS = (\mu_X - \mu_Y)\, d\xi / T$$

$$= A\, d\xi / T, \tag{3.10}$$

where $A = \mu_X - \mu_Y$ is the chemical affinity [2]. The expression (3.10) is the wellknown form of entropy-production for chemical reaction used in irreversible thermodynamics. [1,8].

4. Probability of fluctuation and criteria of stability

The probability distribution $P(A_n) = P(N_1, N_2, \ldots, N_n)$ that results from (2.8) is given by

$$P(N_1, N_2, \ldots, N_n) = \exp\frac{\Delta S}{K} \tag{4.1}$$

where $\Delta S = S - S_{eq} = -K\sum_{i=1}^{n} N_i \ln\frac{N_i}{\bar{N}_i}$ (4.2)

Writing $N_i - \bar{N}_i = \delta N_i$ and assuming δN_i very small, the probability of fluctuation or deviation from the stationary equilibrium state $(\bar{N}_1, \bar{N}_2, \ldots, \bar{N}_n)$ can be reduced to the form of Gaussian law of probability of deviation

$$P(\delta N_1, \delta N_2, \ldots, \delta N_n) = \exp\frac{\delta^2 S}{2K}$$

$$= \exp\left\{-\frac{1}{2}\sum_{i=1}^{n}\frac{(\delta N_i)^2}{\bar{N}_i}\right. \tag{4.3}$$

which was tested for different stochastic models of chemical reaction [9].

Let us now study the significance of the probability of deviation (4.3) for the study of stability of the stationary equilibrium $\{\bar{N}_1, \bar{N}_2, \ldots, \bar{N}_n\}$. We note that the exponent of (4.3), namely,

$$\frac{\delta^2 S}{2K} = -\frac{1}{2}\sum_{i=1}^{n}\frac{(\delta N_i)^2}{\bar{N}_i} < 0 \tag{4.4}$$

which implies that the stationary state $\{\bar{N}_1, \bar{N}_2, \ldots, \bar{N}_n\}$ is more probable than any other neighbouring state $\{N_1, N_2, \ldots, N_n\}$ reached by a small deviation or fluctuation $\{\delta N_1, \delta N_2, \ldots, \delta N_n\}$. This is not, however, sufficient to ensure the stability of the stationary equilibrium state. The positively of the excess entropy-production rate

$$\frac{d}{dt}(\delta^2 S) > 0 \tag{4.5}$$

is necessary in order that the deviation from the steady state can not grow in time. It is when this condition is satisfied, the fluctuation will regress and as such, the system will remain within the domain of attraction So, the criteria of stability of the stationary state $\{\bar{N}_1, \bar{N}_2, ..., \bar{N}_n\}$ as obtained from the consideration of the probability of fluctuation become

$$\delta^2 S < 0, \tag{4.6a}$$

$$\frac{d}{dt}(\delta^2 S) > 0 \tag{4.6b}$$

which are all the same as Lyapunov criteria of stability with $\delta^2 S$ as the Lyapunov function [9].

For the expression (3.10) of entropy-production for chemical reaction, the criterion (4 6a) of stability implies

$$\frac{\partial A}{\partial \xi}(\delta\xi)^2 < 0 \qquad \left.\frac{\partial A}{\partial \xi}\right) < 0 \tag{4.7}$$

which expresses the condition of chemical stability [9].

Let us now study the significance of the second inequality (4 6b). The second condition (4.6b) gives

$$\frac{d}{dt}\frac{1}{2}\sum_{i}^{n}\frac{(\delta N_i)^2}{\bar{N}_i} < 0$$

or, $$\sum_{i=1}^{n}\delta N_i \frac{d}{dt}(\delta N_i) = \sum_{i=1}^{n}\delta N_i \frac{d}{dt}\left(N_i - \bar{N}_i\right)$$

$$= \sum_{i=1}^{n} N_i \delta N_i < 0$$

or $$\dot{N}_i \delta N_i < 0, \quad (i = 1, 2, ..., n) \tag{4.8}$$

which is a generalization of Le-Chatelier-Braun principle of stability for chemical equilibrium. It implies that if a system in stationary chemical equilibrium state undergoes a variation δN_i in any factor characterizing the stationary equilibrium state, a compensating change in the growth rate $\dot{N}_i$ must occur in opposite direction. This principle may thus be adopted as an alternative way of testing stability of a system [10].

5. Conclusion

The paper is an attempt on the probabilistic model of a closed multi-component system. The first result is the derivation of the probability distribution of the molecular numbers $\{N_1, N_2, ..., N_n\}$ of the different components constituting the system. The probability distribution involves the expression for entropy-production whose thermodynamic significance in the context of chemical reaction has been investigated. Finally, the criteria of stability of equilibrium state investigated from the consideration of the probability of fluctuation lead to the criterion of chemical stability and also the generalized Le-Chatelier-Braun principle of chemical equilibrium.

References

[1] E N Yeremin *Fundamentals of Chemical Thermodynamics* (Moscow Mir) (1981)

[2] K Ishida *J Phys Chem* **70** 3806 (1966)

[3] C G Chakrabarti and K De *J Biol Phys* **23** 163 (1997)

[4] ET Jaynes *Phys Rev* **106** 4 (1957)

[5] J N Kapur *Maximum-Entropy Models in Science and Engineering* (New Delhi Wiley-Eastern) (1989)

[6] S Kullback *Information Theory and Statistics* (New York Wiley & Sons) (1959)

[7] S Rice *Statistical Mechanics, Thermodynamics, and Kinetics* (San Francisco Freeman) (1967)

[8] I Prigogine *Introduction to Thermodynamics of Irreversible Processes* (New York Inter Science Publication) (1967)

[9] P Gandsdroft and I Prigogine *Thermodynamic Theory of Structure Stability and Fluctuation* (New York , Wiley-Inter-Science) (1971)

[10] B H Lavenda *Statistical Physics, Probabilistic Approach* (New York Wiley & Sons) (1990)